

Documents Management Branch (HFA-305)  
Food and Drug Administration  
5630 Fishers Lane, Rm 1061  
Rockville, MD 20852

IN RE: Sunscreen Final Monograph

Dear Madam or Sir,

Our comments concern sunscreen photostability and its implications for arriving at a valid UVA testing method and meaningful UVA protection claims.

Our basic premise is that all sun protection derives from radiation attenuation. The Sun Protection Factor (SPF) is primarily a measure of the sunscreen's attenuation of UVB radiation (290-320 nm), and says very little about the sunscreen's attenuation of UVA (320-400 nm). We have conducted *in vitro* testing of many sunscreens. In our experience, a sunscreen with an SPF of 15 attenuates about 94% of UVB radiation, while a sunscreen with an SPF of 30 attenuates about 97%. However, our experience is that even SPF 30 sunscreens may attenuate less than 70% of UVA radiation.

With its erythral endpoint, SPF is easy to measure. Unfortunately, biologically relevant acute responses to UVA are not so clear-cut. There are two biological endpoints under serious discussion as clinical indicators of UVA exposure: Immediate Pigment Darkening (IPD); and Persistent Pigment Darkening (PPD). Both responses require exposure of test subjects to high levels of UVA radiation ( $> 15 \text{ J/cm}^2$ ). Both responses are difficult to observe and require very highly trained technicians to give accurate results. Given the prevailing assumption that exposure to high levels of UVA radiation is deleterious to health, we oppose the use of both clinical methods on both practical and ethical grounds.

Therefore, we support the use of an *in vitro* test method to measure a sunscreen's UVA protection. While we have no great quarrel with the Critical Wavelength method currently under consideration, we think that the simplest, most direct method is the *in vitro* measurement of UVA attenuation expressed as a percent of incident radiation attenuated by a test vehicle.

It is well known that exposure to sunlight degrades the absorbance of some organic UV filters, particularly avobenzene both alone and in combination with ethylhexyl methoxycinnamate and derivatives of amino benzoic acid. Several references to this phenomenon may be found in the accompanying article we recently published, titled "A New Photostabilizer for Full Spectrum Sunscreens." For this reason, we further support the measurement of UVA attenuation following a measured exposure of the test vehicle to solar UV radiation (290-400 nm). Numerous labs have analytical or near analytical protocols designed to measure the ability of a sunscreen to attenuate UVA following UV irradiation. One, which we find acceptable, was developed by Robert Sayre of Rapid Precision Testing Laboratories, Cordova, TN, and described in "Photostability Testing of Avobenzene," a copy of which also accompanies this letter.

We believe that the health of consumers is best served by sunscreens which attenuate as much UVA radiation (320-400) as is practical given current technology and cost considerations. The most effective UVA filter is avobenzene (butyl methoxydibenzoylmethane) which, at its maximum allowable monograph concentration of 3%, will attenuate over 90% of UVA radiation. Avobenzene's attenuation of UVA radiation can be maintained during UV exposure with the addition of a photostabilizer such as octocrylene or diethylhexyl 2,6-naphthalate (see "A New Photostabilizer for Full Spectrum Sunscreens."). Therefore, we think 90% attenuation of UVA merits strong consideration by the Agency as the "gold standard" of effective UVA protection. We submit that a sunscreen which combines 90% attenuation of UVA with 94% or greater attenuation of UVB provides the user with full spectrum UV protection.


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Lastly, we have a recommendation concerning the communication of UVA protection to consumers. Sunscreens which provide at least SPF 15 and attenuate at least 90% of UVA radiation should, in our opinion, be labeled as "Full Spectrum" or as "Providing Full Spectrum UV Protection." By way of explanation, we further recommend that the Agency allow the claim, "Blocks at least 90% of UVA radiation." As consumers cannot recognize UVA damage, we believe that no UVA or broad spectrum or similar claims, be permitted for any sun protection product that doesn't have a minimum SPF of 15.

Thank you for your consideration.

Sincerely,



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# A New Photostabilizer for Full Spectrum Sunscreens

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In this article, we, the authors, advocate a non-traditional approach to sunscreen design, one that aims at providing full spectrum sun protection by attenuating at least 90% of all solar UV radiation. We introduce diethylhexyl 2,6-naphthalate (DEHN)<sup>a</sup>, a new chemical additive for sunscreens developed in the laboratories of C. P. Hall, and we present experimental data showing the photostabilizing effect of this chemical on sunscreens containing the widely-used UV filter, avobenzone. We discuss the photochemistry of sunscreen photostability, the nature of solar irradiance, and the traditional, anti-sunburn approach to sunscreen design. Finally, we present sunscreen formulations that incorporate DEHN and we show the results of both in vitro and in vivo studies of their performance.

## Background

At a time when more people are using more sunscreen than ever before, the lifetime risk of developing malignant melanoma is skyrocketing—more than doubling in the past 20 years to 1 in 74 today.<sup>1</sup> One possible explanation is that, protected from burning, people are prolonging their exposure to longer wavelength UV radiation, known as UVA, which most sunscreens block only partially or hardly at all.<sup>2</sup> Although no causal link has been established between exposure to this radiation and melanoma, the evidence is suggestive and the consensus among doctors is growing that sunscreens should block this radiation

<sup>a</sup> The trade name, HallBrite TQ, is registered to The C. P. Hall Company.

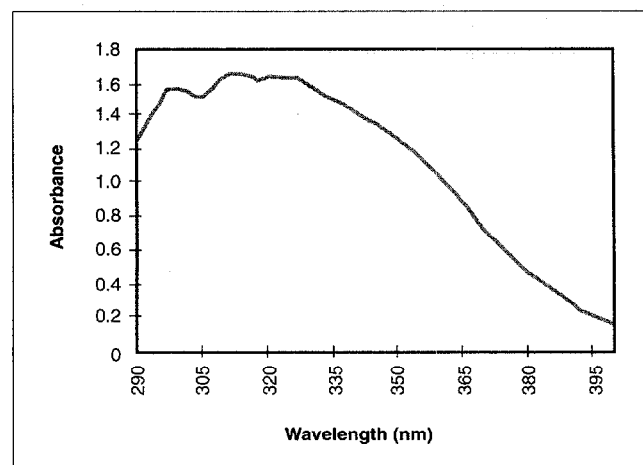


Figure 1. Solar UV absorbance of a traditional SPF 30 sunscreen.

as well.<sup>3,4</sup>

Of the three parts of solar UV radiation, the shorter wavelength UVB portion, from 290 to 320 nm, is regarded as the most deleterious. Direct links have been made between UVB exposure and acute sunburn, mutation induction, immune suppression, cell mortality and skin cancer.<sup>5,9</sup>

But the evidence is now overwhelming that excessive exposure to any part of the solar UV spectrum, including UVA II (320-340 nm) and UVA I (340-400 nm), is harmful. Apart from its possible role in melanoma, UVA has been shown to cause a wide variety of chemical and biological effects including generation of reactive oxygen species, DNA damage, lipid peroxidation, increase in elastin fibers, collagen cross-linking, epidermal thickening, and an increase in the number of dermal cysts.<sup>10-16</sup>

**Full spectrum UV protection:** Traditional sunscreen design focuses on attenuating the sunburn component of UV radiation, principally in the 290 to 320 nm range, sometimes extending to 340 nm (see sidebar on traditional sunscreen design).

In our laboratories, we approach sunscreen design from two simple premises:

- All sun protection derives from UV radiation attenuation.
- The best sun protection derives from radiation attenuation across the entire solar UV spectrum, from 290 nm to 400 nm.

Our objective, therefore, is to facilitate the formulation of sunscreens that reliably attenuate well over 90% of all solar UV radiation. As we see it, sunscreens that perform to this level provide their users with full spectrum protection.

We believe the term "full spectrum" could

## Key words

sunscreen, photostability, triplet energy, avobenzone, UVA

## Abstract

Following irradiation with full spectrum UV, avobenzone sunscreens that contain diethylhexyl 2,6-naphthalate demonstrate improved photostability compared to those without.

Nach Bestrahlung mit Vollspektrum UV-Licht verbesserten Avobenzon-Sonnencremes, die Diethylhexyl 2,6-Naphthalat enthielten, im Vergleich mit Sonnenschutzmitteln ohne Diethylhexyl 2,6-Naphthalat die Photostabilität.

Suite à l'irradiation à rayons ultraviolet à plein spectre, les lotions solaires à l'avobenzone, contenant le diéthylhexyl 2 et le 6-naphthalate, démontrent une photostabilité améliorée comparé aux lotions qui ne contiennent pas ces ingrédients.

Luego de aplicar radiación con todo el espectro de radiación ultravioleta, los filtros solares de avobenzone que contienen naphthalato de diocilo exhibieron mayor fotoestabilidad que aquellos productos que no lo contenían.

## Traditional Sunscreen Design

To most people, sun protection means protection from sunburn. This painful and potentially serious skin injury in light-skinned people is caused by overexposure to solar UV radiation. Indeed, sunscreens are rated by their ability to increase people's tolerance to UV radiation, as measured by the dose required to provoke a slight reddening or erythema, which is the first sign of sunburn. This rating, of course, is the Sun Protection Factor, or SPF. To this day, SPF remains the only meaningful sun protection claim allowed by regulations in the US.

We all know that SPF is imperfect because consumers do not use sunscreens as directed. For example, they don't apply sunscreens at the level mandated in regulatory tests, and they fail to apply sunscreens 30 minutes before going out into the sun. However, SPF is universally accepted and now would be impossible to change. Although run by slightly different methods in different countries, SPF gives about the same results everywhere.

Human studies have shown that the action spectrum for sunburn, known as the erythral action spectrum, is concentrated in the range from 290 to 320 nm with a tail extending out to about 340 nm.<sup>17</sup> Not surprisingly, sunscreens today are designed first and foremost to attenuate the radiation that causes sunburn. This is the so-called UVB portion of the spectrum from 290 to 320 nm. It is not much of an oversimplification to say that the greater the attenuation in this range, the higher the SPF. As SPF requirements increase, sunscreen formulators add absorbance to the right of 320 nm to eliminate the effects of radiation out to 340 nm, often referred to as UVA-II. When attenuation approaches 100% of the radiation between 290 and 320 nm and a significant portion of the radiation from 320 to 340 nm, voila, SPF's of 30 and above are the result. No more sunburn!

Figure 1 shows the absorbance profile of a popular commercial sunscreen with a labeled SPF of 30. One can see that the sunscreen absorbs best in the UVB and short-wave UVA region, but its absorbance trails off in the region of long-wave UVA. Calculations based on the area under the curve indicate that attenuation of UVB is 97% as expected, but attenuation of UVA is only 81%.

solve the question raised at the American Academy of Dermatology Consensus Conference held February 4, 2000. This conference brought the medical, regulatory and scientific communities together to try and reach a consensus on UVA protection by sunscreens. One conclusion was that SPF must remain as a way to advise consumers on UVB protection. The participants also agreed that UVA protection is required in all sunscreens and that a simple label must be developed to show consumers the level of protection.

Because the term "broad spectrum" has been used and mis-used,<sup>22</sup> applying this term to products that protect against both UVB and UVA has become muddled and should be abandoned. We suggest using full spectrum as a permitted claim provided the product attenuates more than 90% of all solar UV

radiation. Products that do not offer this protection could not be labeled as either full spectrum or broad spectrum.

**Achieving full spectrum protection:** Achieving full spectrum protection in a sunscreen requires the incorporation of UV filters that, alone or in combination, absorb throughout the solar UV spectrum. It also requires UV filters that provide the needed magnitude of attenuation within the concentration limits as defined by country regulations and/or cosmetic acceptability (see sidebar on organic UV filters).

A major obstacle to delivering full spectrum protection is the dearth of acceptable UV filters that provide significant attenuation across the entire UVA range from 320 nm to 400 nm. Only avobenzone is currently approved for general use in the US.<sup>b</sup> It absorbs broadly enough and with sufficient magnitude to attenuate more than 90% of UVA radiation. Avobenzone needs help to remain photostable; the very radiation it absorbs can cause it to undergo chemical reactions that degrade its absorbance.<sup>23-25</sup>

## Avobenzone: A Powerful Tool

**Absorbance of UVA and UVB:** When the FDA approved avobenzone for general use in sunscreens in 1997, formulators in the US joined their counterparts in the rest of the world in having available an extremely powerful tool to attenuate UV radiation.<sup>26</sup> The maximum permitted level in the US is 3.0%, in the EU 5.0% and in Japan 10.0%. Unquestionably, in terms of breadth and magnitude of absorbance and its nearly 20-year history of safe use around the world, avobenzone is the leading candidate to extend sun protection throughout the UVA portion of the spectrum.

An often overlooked property of avobenzone is its significant absorbance of UVB (Figure 3). In fact, our data indicates that at 306 nm, avobenzone absorbs almost twice as well on a molar basis as ethylhexyl salicylate (formerly octyl salicylate). At 320 nm, avobenzone's molar absorptivity is about equal to oxybenzone's molar absorptivity at the same wavelength.<sup>27</sup> Avobenzone maintains a significant magnitude of absorbance throughout the UVB band.

**Analyzing sunscreen photostability:** In the laboratory, in vitro experiments were conducted to evaluate the absorbance of various avobenzone formulations both before and after irradiation with 10 MED from a solar simulator.<sup>c</sup> For general reference, 10 MED is equivalent to approximately two hours of sunlight.

Absorbance is defined as  $\log(1/T)$  where T (transmittance) is the ratio of radiation detected after passage through the test vehicle to radiation emitted by a radiation source. Attenuation is defined as  $1-T$ , or, when referred to as a percentage, as  $100(1-T)$ . For reference, absorbance of 2 equals 99% attenuation, absorbance of 1.52 equals 97% attenuation, and absorbance of 1 equals 90% attenuation.

Transmittance data for the sample formulations was obtained by a transmittance analyzer<sup>d</sup>. The analyzer's software<sup>e</sup> integrated the area under the absorbance curve and reported the percentages of radiation attenuation.

Figure 4 illustrates both the promise of avobenzone and its problem. Before irradiation, the 1% avobenzone sunscreen attenuates 75% of the UVB radiation, and 81% of the UVA radiation. Following irradiation, attenuation falls to 57% of UVB and 56% of UVA. Attenuation of UVB is reduced by 24% and attenuation of UVA is reduced by 30% by the 10 MED exposure.

**Photostabilizing with DEHN:** Figure 5 illustrates what happens

<sup>b</sup> Avobenzone is available from several suppliers under the trade names Parsol 1789 (Roche Vitamins, Parsippany, NJ), Solarom BMBM (Frutarom, Haifa Bay, Israel), Neo Heliopan Type 357 (Haarman and Reimer, Holzminden, Germany), Eusolex 9020 (E.Merck, Darmstadt, Germany), and Uvinul BMDM (BASF, Ludwigshafen, Germany)

when DEHN is substituted for another ester in the formula at 4%. Except for the substitution, this formulation is identical in every way to the one depicted in Figure 4. Before irradiation, this formulation attenuates 82% of the UVB radiation and 80% of the UVA. After irradiation with 10 MED, attenuation of UVB is 80% and UVA is 77%. For both UVB and UVA, loss of attenuation is less than 4%.

As we shall see, some very good things happen to sunscreen formulations when avobenzone is formulated with DEHN. But first, let's discuss the chemistry and photochemistry of this material.

## Diethylhexyl 2,6-Naphthalate

DEHN is the diester of 2,6-naphthalene dicarboxylic acid, and 2-ethylhexanol, a branched C8 primary alcohol. Figure 6, on page 40, shows the molecular structure, molecular formula, and molecular weight of DEHN.

The physical properties of this molecule<sup>28</sup> can be inferred to a large extent from its structure. It is a semi-viscous (546 cSt at 25°C by the Kinematic method) liquid at room temperature and has a freeze point of less than 5°C. It has a high refractive index of 1.53. Its specific gravity is 1.02. It is quite lipophilic. It is insoluble in water, propylene glycol and glycerin. It is freely soluble in most oils such as mineral oil, castor oil, and typical cosmetic esters.

Although it may seem unexpected and fortuitous, DEHN is an excellent solvent for lipophilic solids such as the UV filters oxybenzone (benzophenone-3), avobenzone, and ethylhexyl triazone (formerly octyl triazone).

Figure 7 shows the UV absorbance of DEHN. In the solar UV range, it has a peak absorbance ( $\lambda_{max}$ ) of 294 nm and a molar absorptivity ( $\epsilon$ ) of about 9,000. It has two small peaks at 332 and 350 nm, and molar absorptivity at those peaks of about 1,000 and 2,000, respectively.

As shown in Figure 7, on page 40, the solar UV absorbance of DEHN is very weak. By comparison, the absorbance of ethylhexyl methoxycinnamate exceeds .80 at 310 nm, and the absorbance of avobenzone is approximately 1.1 at 355 nm.

The ability of DEHN to photostabilize avobenzone is a function of its capacity to act as an acceptor of triplet energy (see sidebar on photochemistry of photostability). Avobenzone has a triplet energy of about 60 kcal/mol.<sup>29</sup> Based on published values for similar compounds, DEHN has a triplet energy of 57-60 kcal/mol and, therefore, may behave as an acceptor of avobenzone's triplet energy. Work is ongoing to provide a more precise characterization of the photophysical properties of DEHN. Its triplet energy and other properties of interest will be published in due course.

## Sunscreen Applications

Table 2 shows the formulas for several model sunscreens used in the experiments described below. The first two sunscreens, marked A and B, both contain 3% avobenzone, and no other UV filters at all. DEHN has been added to Formula B at 4%, and not to Formula A. So basically we have two matched formulas, a negative control and a positive control.

Figures 9 and 10 show the absorbance profiles of these two formulas before and after 10 MED exposures. It is very important to note that 3%

<sup>c</sup> Model 16S Solar Simulator equipped with a WG 320 filter (transmits UV > 290 nm), output monitored by a PMA 2105 UV-B DCS Detector (biologically weighted) and controlled by a PMA 2100 Automatic Dose Controller (Solar Light Co., Philadelphia, Pennsylvania)

<sup>d</sup> UV1000S UV Transmittance Analyzer, Labsphere Inc., North Sutton, NH

<sup>e</sup> UV1000S Version 1.21, Labsphere Inc. This software uses 290 nm and 315 nm as the limits of the UVB integral rather than the more commonly used 290 and 320 nm. Similarly, the software uses 315 and 400 nm as the limits of the UVA integral.

## Solar UV Irradiance

High-frequency electromagnetic radiation beyond the visible includes UV radiation, X-rays, and gamma rays. All this radiation is ionizing and therefore harmful to body tissues, living cells and DNA.<sup>18</sup>

Of the solar radiation striking the upper atmosphere, about 9% is in the UV wavelength range of 200 to 400 nm.<sup>19</sup> Fortunately, the sun's emissions are highly modified by Earth's atmosphere. Radiation of less than 290 nm is, for practical purposes, eliminated, and radiation from 290 to approximately 400 nm is strongly attenuated. To put that into relevant perspective, the body of a sunbather is struck by  $10^{21}$  photons every second, and about 1% of these are photons of ultraviolet radiation.<sup>20</sup>

Within the UV spectrum itself, the shorter, more energetic wavelengths are the ones most strongly attenuated by the atmosphere. Consequently, of the total UV radiation reaching the surface, the portion between 290 and 320 nm accounts for less than 6%.<sup>21</sup> Figure 2 is a graph of solar UV irradiance recorded in Albuquerque, New Mexico at noon on July 3 and illustrates this important fact.

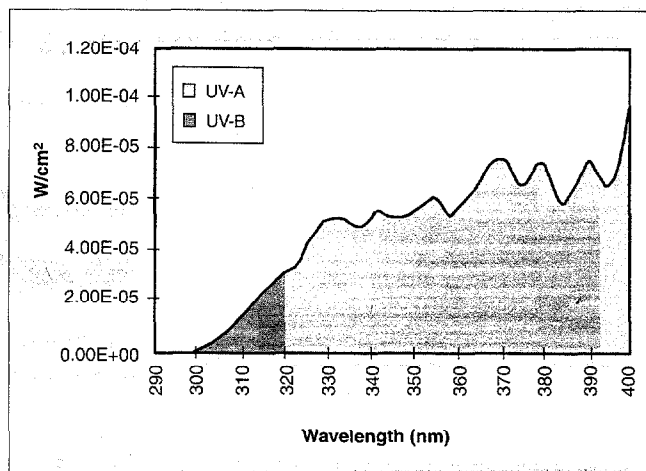


Figure 2. Solar irradiance in Albuquerque, New Mexico, at noon on July 3.

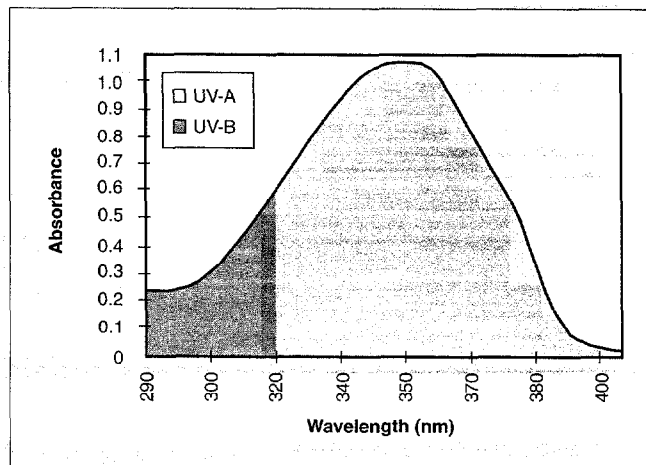


Figure 3. Solar UV absorbance of avobenzone (10 ppm) in cyclohexane.



## Organic UV Filters

Sunscreens contain organic chemicals or metal oxide particles that absorb, reflect, or scatter ultraviolet radiation and prevent it from striking the skin. Most countries regulate these filters by a pre-approval process of creating a positive or permitted list of sunscreen filters. In the C. P. Hall laboratories, research has been limited to organic UV filters, therefore this discussion will be confined to this class of compounds.

Most organic UV filters absorb in a fairly narrow band on either side of their peak absorbance. This band is abbreviated by the symbol  $\lambda_{\text{max}}$  (lambda max). The magnitude of a UV filter's absorbance (its ability to attenuate radiation) is a function of its molar absorptivity at its  $\lambda_{\text{max}}$ , which is abbreviated as the symbol  $\epsilon$  (epsilon). Table 1 lists the most important UV filters approved for general use in the US and in the EU. It indicates their  $\lambda_{\text{max}}$ ,  $\epsilon$ , and maximum permitted concentration by weight in the formulation.

For any solution or sunscreen, it is a fundamental principle of physical chemistry that the magnitude of absorbance is directly proportional to the concentrations of the UV filters present times their molar absorptivity. So, theoretically anyway, a sunscreen's total absorbance is the sum of the absorbances of the individual filters. Formulators can choose from several organic filters that absorb between 290 and about 340 nm, so it's a fairly simple matter for them to combine these in various ways to attenuate the shorter wave portion of the solar UV spectrum.

However, their choices are much more limited when they seek to attenuate the longer wavelengths from 320 to 400 nm. As is readily apparent in Table 1, only menthyl anthranilate and avobenzone absorb near 350 nm, and only avobenzone has the molar absorptivity to attenuate significant radiation at or below its legally allowable maximum concentration.

Table 1. Organic UV filters

	$\lambda_{\text{max}}$	$\epsilon$	US	EU
<b>UVB Filter</b>				
Methylbenzylidene camphor	300	24,500	NA	4%
Homosalate	306	4,300	15%	10
Ethylhexyl salicylate	307	4,900	5	5
Phenylbenzimidazole sulfonic acid	310	28,250	4	8
Ethylhexyl methoxycinnamate	311	23,300	7.5	10
Padimate O	311	27,300	8	8
Ethylhexyl triazone	313	110,000	NA	5
<b>UVB/UVA Filter</b>				
Oxybenzone	288/325	14,000/9,400	6	10
Octocrylene	303	12,600	10	10
<b>UVA Filter</b>				
Menthyl anthranilate	336	5,600	5	NA
Avobenzone	358	34,720	3	5

NA=Not Approved

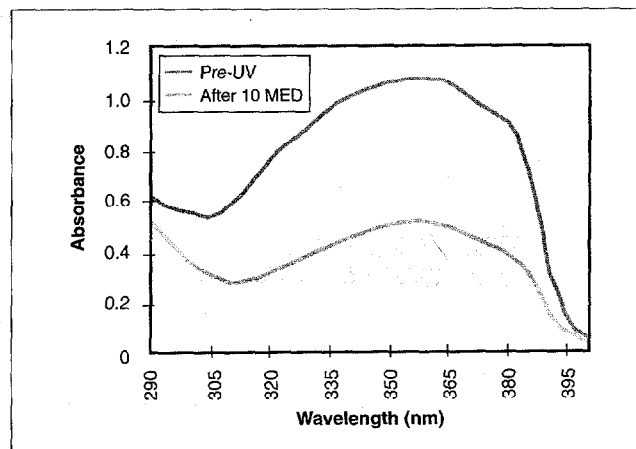


Figure 4. Photostability of a 1% avobenzone formulation with no stabilizer.

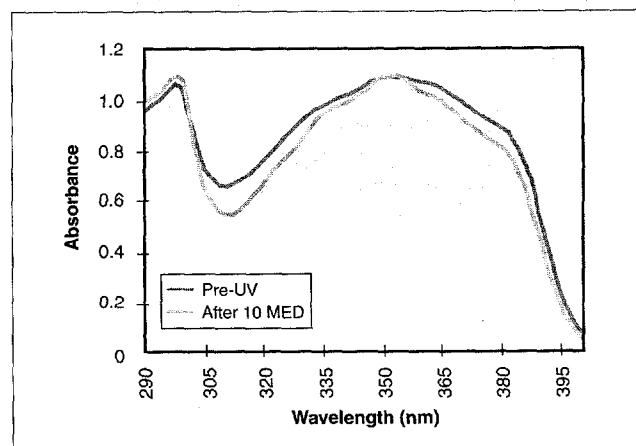


Figure 5. Photostability of a 1% avobenzone formulation with 4% DEHN.

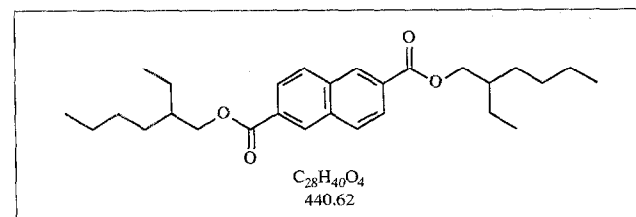


Figure 6. Molecular structure, formula and weight of DEHN. Its CAS Registry Number is 127474-91-3.

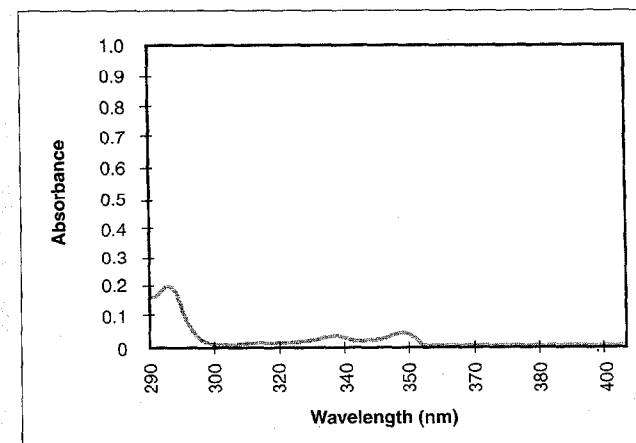
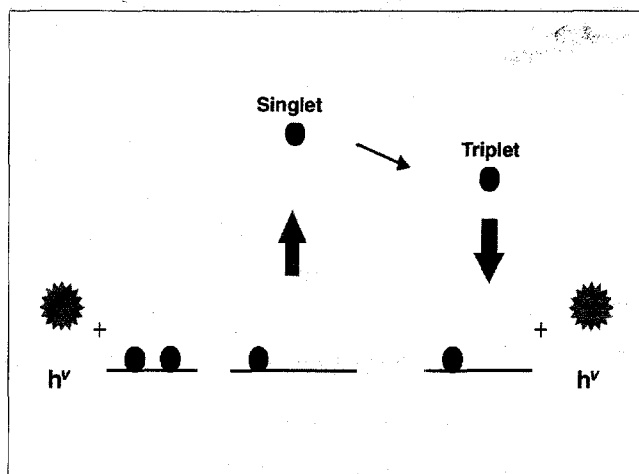


Figure 7. Solar UV absorbance of DEHN (10 ppm) in cyclohexane.



**Figure 8. Schematic representation of photon absorption resulting in the excitation of an electron to the singlet state, the decay to the triplet state, and the emission of a photon before returning to the ground state.**

avobenzone alone attenuates about 90% of all the radiation between 290 and 400 nm. After 10 MED, unfortunately, UVB and UVA attenuation in Formula A, without DEHN, falls to 77% and 64%, respectively. In stark contrast, Formula B, with 4% DEHN, maintains virtually all of its absorbance across the UV spectrum; after 10 MED its UVB attenuation is 92% and its UVA attenuation is 91%. Most importantly for labelling purposes, the formulation which has been stabilized with DEHN delivers an average in vivo SPF of 12 (Table 2).

Once a photostable foundation of 3% avobenzone has been established, it becomes a simple matter to achieve any desired SPF above 10 by adding UVB filters to the formula. Table 2 also shows two more matched formulas, marked C and D, this time adding 5% ethylhexyl salicylate to 3% avobenzone. As you can see in Figure 11, ethylhexyl salicylate increases attenuation of UVB to 94-95% and attenuation of UVA climbs slightly to 93%. After irradiation with 10 MED, however, Formula C without DEHN loses a bit of its UVB attenuation, to 93%, but a lot of its UVA attenuation, falling to 84%. In contrast, Formula D (Figure 12), with 4% DEHN, maintains 94% attenuation of UVB and 92% attenuation of UVA. This level of attenuation adds up to an average in vivo SPF of 17 (Table 2).

Formula E in Table 2 shows a formula to which 4% oxybenzone has been added to the 5% ethylhexyl salicylate and 3% avobenzone and the formulation has been stabilized with 5% DEHN. With oxybenzone's contribution to absorbance in both the UVB and short-wave UVA portions of the spectrum, this formula exhibits significantly increased attenuation across the spectrum, to 97% of UVB and 94% of UVA. Figure 13 shows the absorbance profiles of this formulation before and after irradiation with 25 MED, roughly equivalent to 6 hours in the sun. Most importantly, this photostable formulation delivers an average in vivo SPF of 32 (Table 2).

### Ethylhexyl Methoxycinnamate and Avobenzone

Every technology has its limitations, and the limitation of this photostabilization technology is that it will not completely photostabilize the combination of ethylhexyl methoxycinnamate (formerly octyl methoxycinnamate) and avobenzone. It can, however, help formulations containing this combination, as illustrated in Figures 14 and 15.

### Photochemistry of Photostability

To begin at the beginning: a photon is a quantum or "packet" of electromagnetic energy with an energy equal to Planck's constant ( $h$ ) times its frequency ( $\nu$ ). The absorption of a photon by an organic molecule causes the excitation of one of a pair of electrons in a low energy orbital to a higher energy unoccupied orbital (Figure 8).<sup>30</sup>

Before absorption, the orbital configuration of the electrons is the "ground" state. Upon absorption, two electronic states are possible. In one, the spins of the two electrons remain paired and, as in the ground state, the net spin of the pair is zero. This is called the "singlet" excited state. In the other, the spins of the two electrons are unpaired, and there is a net spin. This is called a "triplet" excited state because three states can be resolved in a magnetic field.<sup>31</sup>

The energy of both excited states is eventually dissipated as heat (vibration, including both bond stretching and nuclear motion), or heat and light (emission of a photon of lower energy/longer wavelength). Emission of a photon from the singlet state is called "fluorescence." Photon emission from the triplet state is called "phosphorescence." The singlet state may return to the ground state directly, or it may decay to the triplet state.<sup>32</sup>

The singlet state is often short-lived, typically  $10^{-8}$  to  $10^{-9}$  seconds. Therefore, reactions that proceed from it must be quite rapid. Of more importance to the sunscreen formulator are reactions that proceed from the (usually) much longer-lived triplet state, which may last  $10^{-4}$  seconds or longer.<sup>33</sup>

During the triplet state lifetime, the excited molecule looks and behaves as a diradical,<sup>34</sup> from which many chemical reactions are possible. In general, these reactions can be grouped into four categories: photoaddition/substitution, cycloaddition, isomerization, and photofragmentation.<sup>35-36</sup> Of particular importance to the sunscreen formulator are reactions between like or different UV filter molecules, those between UV filter molecules and sunscreen excipients, and isomerizations or fragmentations of the UV filter molecules. Any one of these reactions may alter or destroy the UV absorption capacity of the sunscreen formulation.

The excited molecule may react (to produce isomers or new products), or return to the ground state in its original form. Clearly, the latter is the preferred outcome for sunscreen formulators (and users) because, among other reasons, the UV filter molecule is again available to absorb a photon.

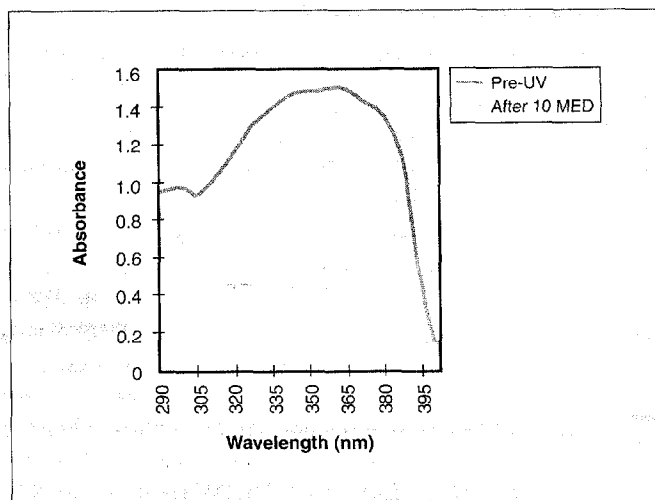
Many factors determine the pathway an excited molecule will take. Among these factors are the triplet energy, the triplet lifetime, the identity and concentration of the reactants, and the rates and activation energies of each competing reaction. Under certain conditions, the excited molecule may return to the ground state (and its original form) by transferring its energy to a nearby molecule. The excited molecule becomes a "donor" and the nearby molecule becomes an "acceptor." Upon the transfer of energy, the donor returns to ground state and the acceptor is elevated to the excited state.<sup>30</sup>



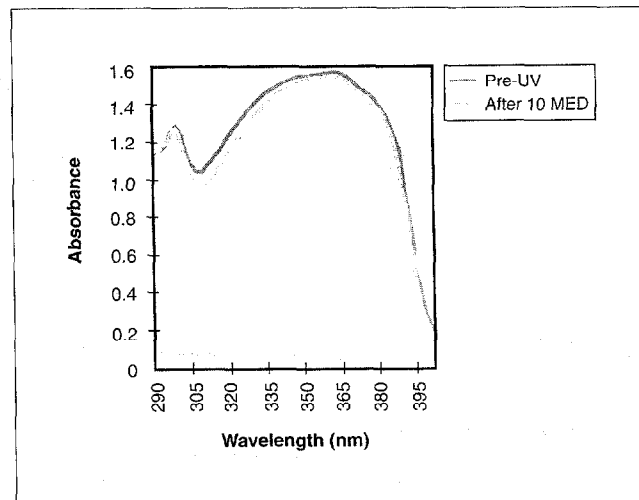
**Table 2. Formulas for model sunscreens used in photostability experiments**

Ingredient	A	B	C	D	E	F
<b>Oil Phase</b>						
Avobenzene	3.0%	3.0%	3.0%	3.0%	3.0%	3.0%
Ethylhexyl salicylate			5.0	5.0	5.0	2.0
Oxybenzone					4.0	2.8
Ethylhexyl methoxycinnamate						5.2
Diethylhexyl naphthalate		4.0		4.0	5.0	7.5
Isopropyl myristate	8.0	4.0	4.0		4.0	1.0
Hexyldecyl benzoate (and) butyloctyl benzoate	7.5	7.5	6.5	6.5	4.5	
Stearyl alcohol	0.3	0.3	0.3	0.3	0.3	0.3
PPG-2 myristyl ether propionate	1.0	1.0	1.0	1.0	0.5	
Polyglyceryl-3 methyl glucose distearate	3.0	3.0	3.0	3.0	3.0	3.0
C30-38 Olefin/isopropyl maleate/MA copolymer	1.0	1.0	1.0	1.0	1.0	1.0
<b>Water Phase</b>						
Water ( <i>aqua</i> )	qs	qs	qs	qs	qs	qs
Disodium EDTA	0.05	0.05	0.05	0.05	0.05	0.05
Glycerin	4.0	4.0	4.0	4.0	4.0	4.0
Butylene glycol	2.0	2.0	2.0	2.0	2.0	2.0
Phenoxyoxythenol (and) methylparaben (and) ethylparaben (and) propylparaben (and) butylparaben	0.7	0.7	0.7	0.7	0.7	0.7
Carbomer	0.2	0.2	0.2	0.2	0.2	0.2
Triethanolamine	0.2	0.2	0.2	0.2	0.2	0.2
<i>in vivo</i> static SPF*	6.3(6)	12.1(10)	13.0(10)	17.3(16)	32.8(30)	NA

\*Studies conducted on five human test subjects by Consumer Product Testing Company, Fairfield, NJ. First value given is the average of the five scores. Value in parentheses is the lowest of the five scores.



**Figure 9. Photostability of Formula A (after 10 MED): 3% avobenzene formulation with no stabilizer.**



**Figure 10. Photostability of Formula B (after 10 MED): 3% avobenzene formulation with 4% DEHN.**



In this experiment, a commercial sunscreen and a close equivalent model sunscreen stabilized with 7.5% DEHN were exposed to 5 hours of sunlight side-by-side on a hot summer's day in Chicago. Before exposure, both sunscreens demonstrated an in vitro SPF of 50. Both also exhibited 97% attenuation of UVB and 95% attenuation of UVA. After 5 hours of sunlight, the commercial sunscreen declined in attenuation to 95% UVB and 84% UVA, and to SPF 26 (Figure 14); the stabilized model sunscreen maintained attenuation of UVB at 97% and declined in attenuation of UVA to 87%, and to SPF 36 (Figure 15). This is approximately a 40% improvement in SPF stability.

The most stable sunscreens, however, are achieved by adding DEHN to avobenzone, and leaving out the ethylhexyl methoxycinnamate. This is one of our suggestions for formulating with DEHN (see sidebar presenting guidelines for formulating with DEHN).

## Conclusion

Unquestionably, people with light skin are best served by sunscreens that attenuate radiation across the entire solar UV spectrum, 290-400 nm. Sunscreens that provide at least 90% attenuation over the entire UV spectrum are deserving, in our opinion, of being called full spectrum sunscreens.

We have presented just a few of the many formulations and allowed UV filter combinations (from the US and Europe) that can be used to achieve full spectrum protection. The key to all of them is the establishment of a photostable foundation on the UVA side of the spectrum. The combination of avobenzone and the photostabilizer diethylhexyl 2,6-naphthalate provides a photostable foundation that can, when properly formulated, attenuate more than 90% of both UVB and UVA radiation. Once that's done, UVB attenuation can be staged to give consumers their choice of the level of sun protection they want, as measured by SPF.

We should add that, in our experience to date, the inclusion of diethylhexyl 2,6-naphthalate improves the performance of every sunscreen, regardless of the UV filter combination.

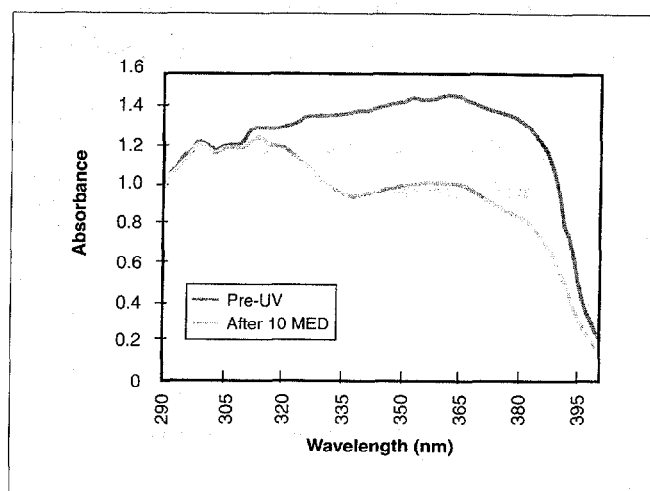
**Acknowledgment:** The authors gratefully acknowledge the valuable contributions of Peter Marinelli, Mark Miller, Yin Hessefort and Gary Wentworth, all of The C. P. Hall Company, and Kerry Hanson, of the University of Illinois.

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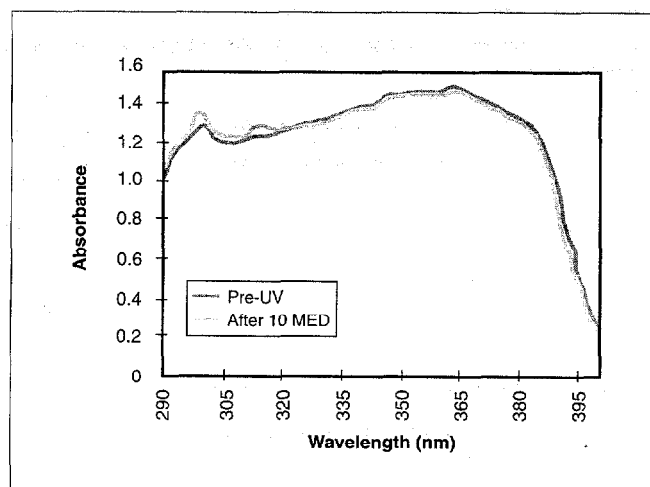
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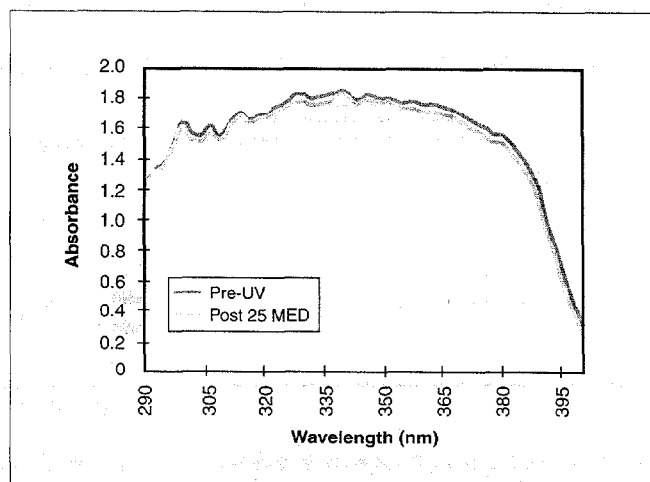
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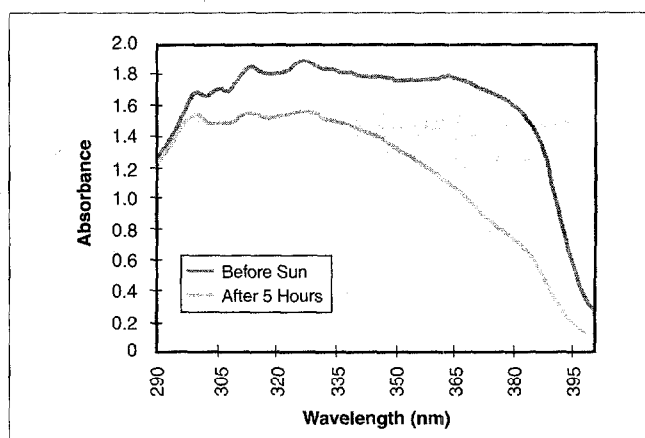
**Figure 11. Photostability of Formula C (after 10 MED): 5% ethylhexyl salicylate and 3% avobenzone formulation with no stabilizer.**



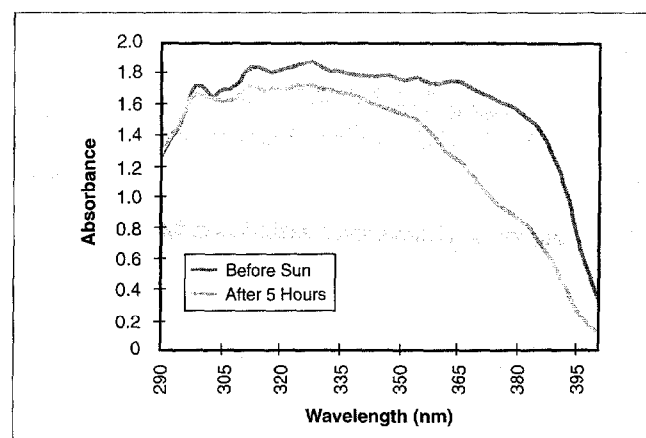
**Figure 12. Photostability of Formula D (after 10 MED): 5% ethylhexyl salicylate and 3% avobenzone formulation with 4% DEHN.**



**Figure 13. Photostability of Formula E (after 25 MED): 5% ethylhexyl salicylate, 4% oxybenzone, 3% avobenzone with 4% DEHN.**



**Figure 14. Photostability of an SPF 30+ commercial sunscreen (after 5 hours in the sun) with ethylhexyl methoxycinnamate and avobenzone.**



**Figure 15. Photostability of an SPF 30+ commercial sunscreen (after 5 hours in the sun) with ethylhexyl methoxycinnamate, avobenzone and DEHN.**

### Guidelines for Formulating with DEHN

1. Compatibility and aesthetics: DEHN is compatible with most lipophilic cosmetic ingredients. Add it to the oil phase as you would any liquid ester. DEHN is fairly viscous, so blending it with lighter oils such as butyloctyl salicylate, isopropyl myristate, and C12-15 alkyl benzoates will insure spreadability and an elegant skin feel.
2. Solvency: DEHN is an excellent solvent, at least 17% w/w, for avobenzone, oxybenzone and ethylhexyl triazone, and it will reduce the need for other solvents in the oil phase. However, make sure that your oil phase has sufficient capacity to dissolve the other sunscreens completely. As a rule of thumb, include 4.5 times as much oil as solids. To make sure the solids will not precipitate out after dissolution, set aside a small aliquot to observe over several days or longer.
3. UV Filter combinations: DEHN is a photostabilizer for avobenzone and, to a lesser extent, for oxybenzone. For optimal stabilization of avobenzone, DEHN should be used in a ratio of 4:3 or greater. For example, 3% avobenzone requires at least 4% DEHN. More will generally confer greater photostability. DEHN will not photostabilize avobenzone in the presence of ethylhexyl methoxycinnamate, though it does improve the photostability of this combination. When formulating FDA-compliant sunscreens, the most photostable systems combine DEHN, avobenzone, oxybenzone, ethylhexyl salicylate, and/or homosalate. You can achieve the entire SPF range, from below 10 to 30-plus, with combinations of these UV filters. For example, 3% avobenzone stabilized with 4% DEHN gives an SPF 10. Adding 5% ethylhexyl salicylate to that provides an SPF 16. Adding 4% oxybenzone to that and increasing DEHN to 5% provides SPF 32. For European sunscreens, DEHN, ethylhexyl triazone and avobenzone perform very well. DEHN also improves the performance of ethylhexyl methoxycinnamate and benzophenone-3 in combination, in the absence of avobenzone.

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U.S. Patent Number 5,993,789  
PRODUCT INFORMATION SHEET

## HallBrite® TQ™

INCI Name: Diethylhexyl 2,6-naphthalate

CAS No. 127474-91-3

### Description

HallBrite TQ is a multifunctional (sunscreen and color stabilizer, solvent, emollient, glossifier, formulation aid for clear systems), synthetically produced diester of 2,6-Naphthalenedicarboxylic acid and 2-Ethylhexanol. The resulting semi-viscous oil is suitable for use as an additive in sunscreens, creams, lotions, antiperspirant sticks and gels, and topical preparations for skin and hair. HallBrite TQ is a powerful photostabilizer for Avobenzone (Parsol® 1789, Roche) by the mechanism of triplet-triplet energy transfer. The ability of HallBrite TQ to "quench" triplet energy provides formulators with a new tool to create photostable broad spectrum sunscreens that achieve much higher Sun Protection Factors with the same or lower levels of active ingredients. By the same mechanism, HallBrite TQ may be used alone or in combination with other UV sunfilters to stabilize makeup color and hair color, both natural and dyed. With its high refractive index, it may be used to add gloss to skin and hair. The same property makes it particularly useful for raising the refractive index of silicone oils to produce clear sticks and gels. It is compatible with most lipophilic cosmetic additives, and solubilizes many commonly used active ingredients including Oxybenzone, Avobenzone, and Octyl triazone. Recommended use level is 2-8%.

### Technical Data

Molecular Weight: 440

Typical Properties (not to be used for specifications):

Appearance:	Clear liquid
Acid Value:	<1
Odor:	Practically odorless
Color:	White to pale yellow (APHA 50)
Refractive Index:	1.533
Specific Gravity:	1.0202
Purity:	98%-plus

### Properties

Sunscreen stabilizer, solubilizer for sunscreen actives Oxybenzone, Avobenzone, and Octyl triazone, photostabilizes Avobenzone, boosts SPF, glossifier, stabilizes makeup color, stabilizes hair color, formulation aid for clear sticks/gels

### Applications

Sunscreens, creams and lotions, hair sprays and conditioners, colored makeup, lipstick, clear antiperspirant sticks/gels

### Toxicology Profile

Repeated Insult Patch Test:	Did not indicate any clinically significant potential for irritation or allergic contact sensitization
Phototoxicity (Guinea pigs):	Not a phototoxin
Photoallergenicity (Guinea pigs):	Not a photoallergen
Ames Test:	Not a mutagen
Acute Oral Toxicity:	LD <sub>50</sub> > 5g/kg
Acute Dermal Toxicity:	LD <sub>50</sub> > 2g/kg
Primary Dermal Irritation:	Minimal or no erythema at 72 hours (Category IV)
Primary Ocular Irritation:	Irritation clearing in 8-21 days. No corneal involvement (Category II)

### Solubility

Solvency of:	Soluble in:	Insoluble in:
Oxybenzone(17% w/w)	Mineral oil	Glycerin
Avobenzone (18% w/w)	Isopropyl myristate	Water
Octyl triazone(20% w/w)	Cyclomethicone	
	Capric/caprylic triglyceride	
	Octyl methoxycinnamate	



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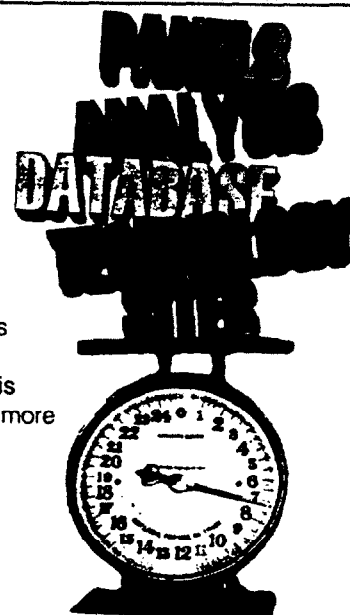
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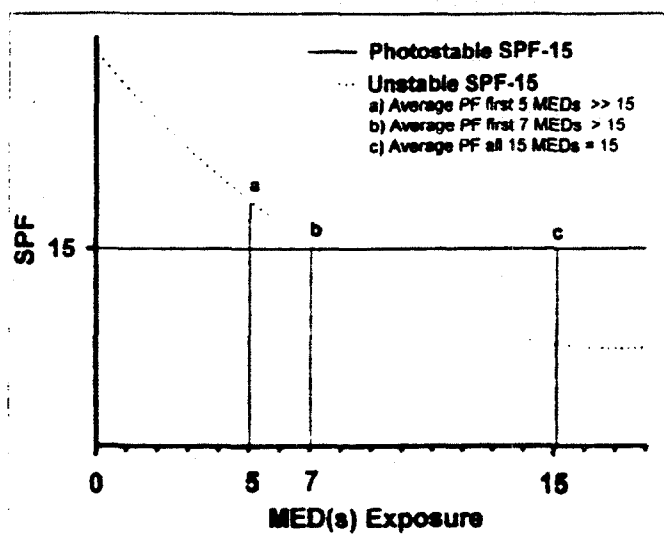


Figure 6. Typical photodegradation curve. (Modified from Pettit and Gonzenbach)

This figure shows how photounstable products initially provide better protection than claimed. As photodegradation proceeds, unstable products lose protective capability. By the time the SPF exposure is reached, considerably less protection than claimed still remains. If overexposed, consumers will sunburn worse "through" unstable products than stable ones of the same SPF. This also explains why, in certain studies, avobenzone products appeared to be so effective. In one such study, mice treated with SPF-15 products were exposed to 5 to 7 MEDs. Because the unstable product was only partially degraded, the average PF was higher than claimed, and the formula appeared more protective compared to a photostable product with the same SPF.

significantly serious. For a photounstable SPF 15 product whose protection has degraded to the extent shown by product A (Figure 4), a 19 MED exposure will result in a severe 4 or 5 MED sunburn.

**Other studies:** Parts of this work have been presented at two recent scientific meetings: the 1998 Photomedicine Society meeting<sup>17</sup> and the 1998 American Society for Photobiology meeting.<sup>18</sup> At both events, participants from pharmaceutical and personal-care manufacturers asked essentially the same question: Why did the work of Dr. L. Kligman and colleagues<sup>19</sup> indicate that an avobenzone-containing product was more effective than an avobenzone-free product of the same SPF after UV exposures were administered? This is a valid question. The Kligman et al. study shows that an SPF 15 with avobenzone provided superior protection to non-avobenzone SPF 15 products, compared the products using 5 to 7 MED exposures.

We understand the SPF of a product is defined by an endpoint of a 1 MED burn

delivered through the product. Stable products provide the same amount of protection throughout the entire duration of the exposure, while photounstable products provide a decreasing amount of protection over the exposure. Since photounstable products have a defined SPF, when the test begins, the product must initially be substantially more protective than the SPF indicates. This dynamic, illustrated in Figure 6 (a modification of an earlier figure proposed by Gonzenbach and Pittet<sup>20</sup>), shows that when fractional exposures are administered using less than the SPF indicated, the protection provided is significantly greater. Therefore, the comparison in the study made at 5 to 7 MED was not relevant for consumers requiring a full SPF 15 protection. The practical difference for consumers is that, with photounstable products, once the SPF is exceeded, more severe sunburns may result than would occur with photostable products of the same SPF.

**Formulators' challenge:** Formulators have a challenge facing them: based on this study, we advise awareness to these results when formulating products that include avobenzone in combination with UVB sunscreens. In Figure 3, one can observe that, at 360 nm, 3% avobenzone in a product has 75% of the maximum MPF that the other 10.5% of UVB sunscreen agents exhibit at 310 nm. Clearly, a small amount of avobenzone has the potential to provide a significant amount of protection and could be extraordinarily effective and beneficial for consumers.

While other studies examining the stability of avobenzone are needed, based on our results, we believe two hurdles need to be addressed to develop photostable avobenzone-containing products. First, formulators need to be aware that avobenzone could make other UVB sunscreens photounstable; simply adding avobenzone to an established product may potentially decrease the SPF due to this loss of UVB protection. There may be combinations of UVB sunscreens and avobenzone that minimize or prevent this interaction. Additionally there may be stabilizer molecules which, if added to formulations, could alleviate this potential difficulty and better stabilize the product. A second potential hurdle is to prevent photodecomposition of avobenzone itself; again there may be stabilizer or quencher ingredients that could block or retard this possible effect.

There are good reasons why formulators should address these challenges head-on. Clearly, any formula that is photostable will have a significant advantage over other competitive products, because avobenzone is a very potent-absorbing compound, a formulator should be able to produce very high SPFs with less active ingredients. The resulting stable formula, using fewer sunscreens at low concentrations, should result in competitive pricing. Also, because avobenzone is such a potent UVA sunscreen, a photostable product containing it should be more effective in clinical tests, especially involving UVA-rich sunlight.

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 \* CDM, Ten Berge, CHP, Bruins, and J.S. Faber, Die Photochemie van

## Discussion

These results show that sunscreen products containing avobenzone may experience photodegradation from UV exposures. Our study also suggests that octyl methoxycinnamate and padimate O, normally shown to be photostable UVB sunscreens, did not show such effectiveness in the products containing avobenzone (Figure 3). Further studies of this are warranted to determine if avobenzone (the ingredient) or the formulations (the methods of using avobenzone) can cause photosensitized degradation of other sunscreen ingredients, as products containing either padimate O or octyl methoxycinnamate without avobenzone appear photostable in this study.

**UVB unrelated:** When we removed the UVB radiation from our system using a 2 mm WG-360 filter, the photodegradation of avobenzone occurred with as little as 0.2 MED of UVA exposure, suggesting that UVB is not required to cause photolysis of avobenzone.<sup>17,18</sup> As the amount of UVB increased in the spectrum, the total amount of UVA decreases for each MED administered. Sources with more UVA-1 (340 to 400 nm) radiation could destroy avobenzone faster than sources with less UVA-1. Therefore, we believe the precise number of MEDs required to destroy the available avobenzone depends on the amount of UVA-1 in the source.

**Sunlight vs. solar simulator:** Figure 4 shows the fraction of protection remaining based on the change in average MPF during exposure of a product film. For each product we tested, the majority of loss of protection appears to have occurred by a 2 or 3 MED exposure. We setup our exposure system to spectrally resemble sunlight (Figure 5) in that it has the full complement of UVA-1 (340-400 nm) radiation that is available in sunlight. While the intensity of our system is similar to sunlight, it is lower than the intensity of other solar simulators commonly used in SPF testing. In sunlight, a fair-skinned individual's MED might be 15 to 20 min. The estimated MED for our source is 10 to 15 min, rather than 10 to 15 sec commonly used for in vivo sunscreen testing.

As Figure 5 shows, our solar simulator, like sunlight, has considerably less short UVB radiation per MED than solar simulators commonly used in sunscreen testing. Regarding UVA photostability, this means that, in sunlight, an individual is exposed to 6 to 15 J/cm<sup>2</sup> of broad-spectrum UV per MED, mostly UVA. Conversely, when using conventionally filtered solar simulators to test SPF, a volunteer is exposed to only 1 or 2 J/cm<sup>2</sup> of UV per MED, mostly UVB with little UVA. Because sunlight is so rich in UVA, compared to solar simulators used in SPF testing, sunscreen UVA photostability may not be adequately accounted for in the current SPF test in the US.<sup>19</sup>

In clinical SPF testing, it is customary to have the expected SPF spaced as the center exposure in a sequence. For instance, to test an SPF 15 product, the center exposure is 15 MEDs, the next exposure is 19 MEDs and the last exposure is 23 MEDs. For a photostable SPF 15 product, the 19 MED exposure causes a 1.27 MED burn and the full 23 MED exposure produces a sunburn of 1.53 MED. Sunburns less than 2 MEDs are not

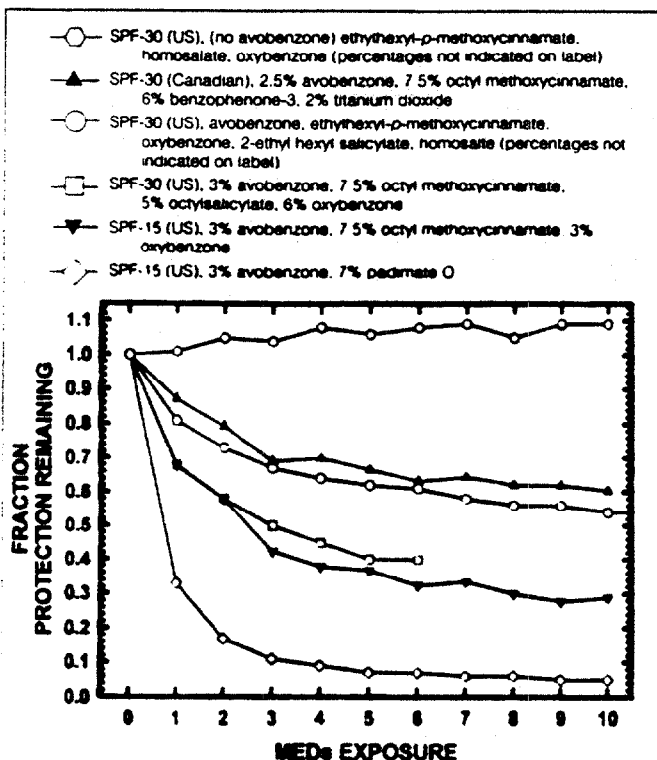


Figure 4. Change in average monochromatic protection factor with UV exposure.

The average monochromatic protection factor is calculated for each formula (Average MPF =  $\text{Sum MPF} / \text{Sum} \lambda$ ). Each point represents the average MPF after the exposure to that point. It is shown as fraction of the protection remaining. Note that, by 2 or 3 MEDs exposure, all available avobenzone has been photodegraded. At this point, only UV-stable sunscreens remain available in the product. This figure shows the data for a selection of formulas tested. Note the SPF 30 product which does not contain avobenzone whose protection remains constant throughout exposure.

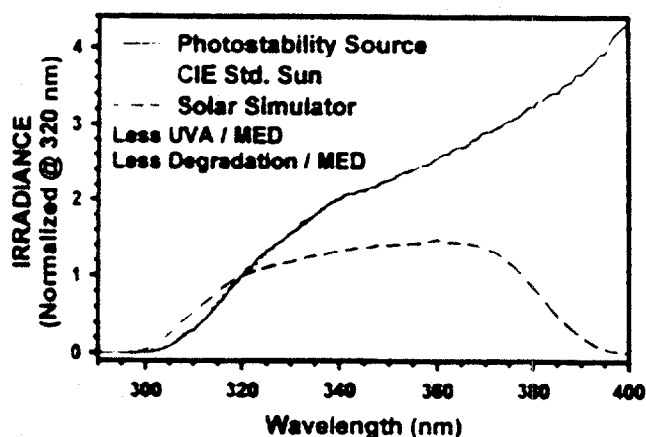


Figure 5. Comparison of sunlight, our solar simulator and standard human test solar simulator.

The typical solar simulator used to determine the SPF of sunscreen products meets existing FDA and COLIPA standards. This solar simulator has more short UVB radiation than is present in sunlight and has less than half of the UVA-1 (340-400 nm) intensity available in sunlight.

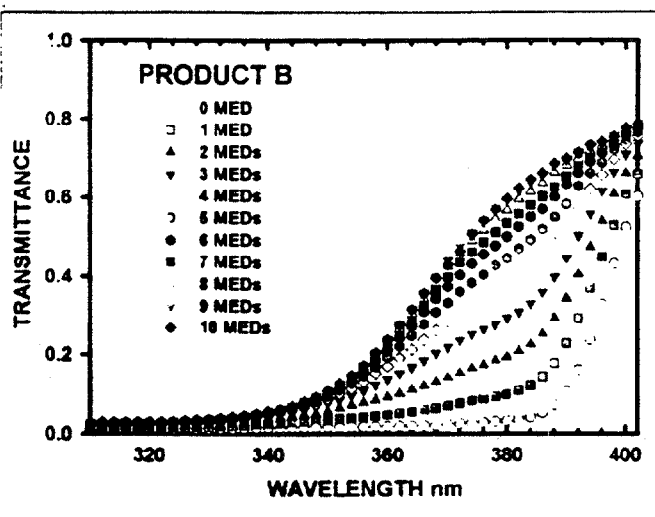


Figure 2. Transmittance of avobenzone-containing product. The transmittance of the sunscreen applied to a Teflon film is measured periodically during UV exposure at each MED increment. Note the UVA transmittance increases with increasing exposure. While changes in the UVB protection are evident, the magnitude is not apparent.

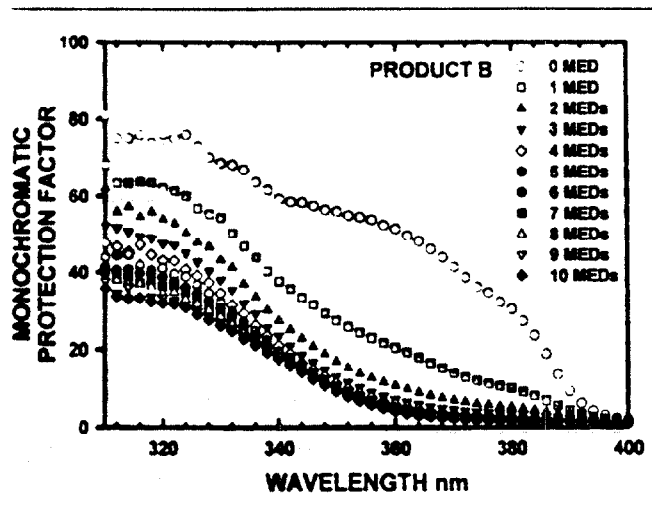


Figure 3. Change in monochromatic protection factor (MPF) with UV exposure.

Many laboratories use monochromatic protection factor representation to analyze sunscreen efficacy. The monochromatic protection factor  $MPF = 1/T$ , where  $T$  is the transmittance of the sunscreen formula. Note the loss of MPF in the UVA-I ( $\lambda > 340$  nm). After 1 or 3 MEDs exposure, UVA-I protection provided is trivial. Also note the significant decrease in the monochromatic protection in the UVB. Avobenzone contributes less than 10% of the monochromatic protection in the UVB, but the decrease in monochromatic protection is 30% after 2 MEDs and approaches 50% by 10 MEDs. The UVB sunscreens are being changed. The potential protection provided by avobenzone is clearly shown in this plot. At 360 nm before irradiation, the MPF due to 3% avobenzone is ~5% of the UVB MPF (300-320 nm) of the other 10.5% UVB sunscreens. After 10 MEDs exposure, the MPF at 360 nm is about 10% that of the remaining UVB sunscreens at 300-320 nm.

light guide coupled to the integrating sphere, so that transmittance measurements of the sunscreen films could be made while continuously exposing the film to full-spectrum, solar-simulated radiation.

We programmed the spectroradiometer to measure the initial product transmittance and then automatically remeasure the transmittance of the film at 1-MED intervals throughout the exposure period. For each specimen, an array of transmittance measurements resulted, beginning with the unexposed product and proceeding through a series of multiple MED exposures.

**Products tested:** A series of sunscreen products currently marketed in North America were examined:

- A. SPF-15 (US), 3% avobenzone, 7% padimate O
- B. SPF-15 (US), 3% avobenzone, 7.5% octyl methoxycinnamate, 3% oxybenzone
- C. SPF-30 (US), avobenzone, ethylhexyl-*p*-methoxycinnamate, oxybenzone, 2-ethyl hexyl salicylate, homosalate (percentages not indicated on label)
- D. SPF-30 (Canadian), 2.5% avobenzone, 7.5% octyl methoxycinnamate, 6% benzophenone-3, 2% titanium dioxide
- E. SPF-30 (US), 3% avobenzone, 7.5% octyl methoxycinnamate, 5% octylsalicylate, 6% oxybenzone
- F. SPF-30 (US), (no avobenzone) ethylhexyl-*p*-methoxycinnamate, homosalate, oxybenzone (percentages not indicated on label)

## Results

The results of the data analysis were viewed in three formats:

1. Film transmittance for each MED exposure interval (Figure 2);
2. Monochromatic protection factors (MPF) (Figure 3). The MPF is the reciprocal of the transmittance;
3. Changes in product performance, shown as the remaining fraction of the initial average MPF (Figure 4).

Figure 2 shows how the transmittance spectrum of an avobenzone-containing formula changes with UV exposure. In this representation, we discovered increased transmittance as the products photodegrade. When this data was expressed as MPF (Figure 3), we found that a considerable loss of protection occurred within the first two MED exposures. While most of this degradation occurred in the UVA spectrum, loss throughout the entire spectrum was also observed. Changes are apparent in the UVB portion of this plot. The degree of these changes, in light that they do not occur when avobenzone is absent in the formulation, suggests that the UVB sunscreen(s) may be degraded by an avobenzone-photosensitized mechanism.

Our work, encompassing an examination of products containing avobenzone that we obtained on the US and Canadian markets, found that this ingredient showed photostability. Figure 4 shows how the fraction protection remaining of the initial average MPF changes with increased exposure. Note that Product F, which does not contain avobenzone, appears to be photostable throughout the duration of exposure.



# Photostability Testing of Avobenzone

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Photostability studies usually involve the examination of the photochemical degradation of a specific chromophore, and most work generally focuses on issues regarding the detection and analytical measurement of the degradation of sunscreen agents.<sup>1-6</sup> Work on photostability in the 1970s and 1980s focused on cinnamates, benzoates and benzilidene camphor sunscreen derivatives.<sup>1-6</sup> More recently, sunscreen photostability studies have emphasized di-benzoyl methane derivatives but have not systematically examined films of products.<sup>11-16</sup> In this study, we tried to duplicate as closely as possible real sun exposure to dynamically assess the photostability of sunscreen drug products.<sup>17-18</sup> Recently, Maier et al. investigated similar sunscreen products and reported comparable findings.<sup>19</sup>

This study focuses on some implications of photostability relative to the efficacy of sunscreen products. Photo-safety testing is used to ensure that formulations, including common

photo-breakdown products, are safe. However, no practical amount of testing can ensure that an undesirable photointeraction will not result when other topical products are used in conjunction with a photoreactive sunscreen formula.

## Methods

For this study, we devised an apparatus and an analysis technique designed to dynamically assess the photostability of sunscreen drug products exposed to a solar-like radiation source. The experimental setup simultaneously irradiates and monitors changes in the transmittance of films of sunscreen products in place without disturbing the sample in the beam (Figure 1).

Initially the solar simulator, using a 1 mm WG-320 filter,<sup>4</sup> was measured using the spectroradiometer calibrated in irradiance mode to determine the MED. For this study, a MED is defined as 20 mJ/cm<sup>2</sup> of erythemically effective exposure. The same spectroradiometer was then calibrated against the solar simulator source for transmittance measurements with a UV transparent Teflon membrane mounted in the entrance aperture of the integrating sphere.

Thin films of sunscreen products, about 1 to 2mg/cm<sup>2</sup>, were then applied to the Teflon membranes and positioned in the entrance to the integrating sphere. Exposures were administered through the liquid

## Key words

photostability,  
avobenzone,  
sunscreens, testing,  
photodegradation

## Abstract

This study investigates the photostability of avobenzone by measuring various sunscreen products. The authors suggest some areas to overcome in formulating.

In dieser Studie wird die Photostabilität von Avobenzon durch Messung verschiedener Sonnenschutzmittel untersucht. Die Autoren diskutieren Formulierungsprobleme

Cette étude examine la photostabilité de l'Avobenzon en procédant à l'évaluation de différents produits filtrants. Les auteurs suggèrent quelques idées maitriser sa formulation.

En este estudio se investiga la fotoestabilidad de la avobenzona mediante el análisis de diversos productos para protección solar. Los autores sugieren algunos problemas que deben superarse durante la formulación

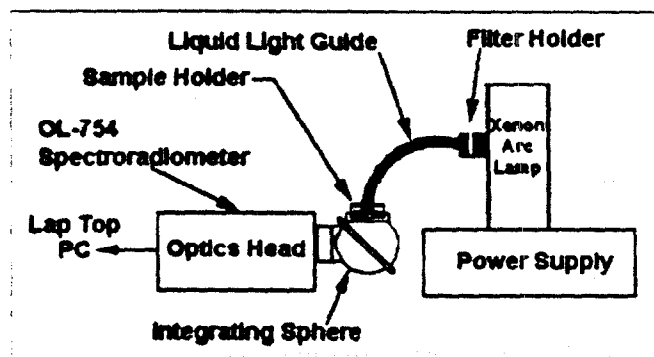


Figure 1. Schematic of photostability test system.

The OL-754 spectroradiometer is used in two modes. It is used in irradiance mode to measure the spectrum of the filtered solar simulator, and it is used in transmittance mode to measure the UV transmittance of the sunscreen film being irradiated. A 150-watt xenon arc is filtered to achieve a solar-like spectrum using a Schott 1 mm WG-320 filter. Radiation is conveyed to the sunscreen applied to a Teflon film mounted in the integrating sphere via the fiber optic light guide. All transmittance measurements are made automatically without moving the Teflon membrane/product film mounted in the integrating sphere.

<sup>4</sup>Schott WG-320, Schott Glass Technologies Inc., Duryea, PA, USA